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An Enantioselective Synthetic Route toward Second-Generation Light-Driven Rotary Molecular Motors

Pijper, Thomas C.; Pijper, Dirk; Pollard, Michael M.; Dumur, Frederic; Davey, Stephen G.; Meetsma, Auke; Feringa, Ben L.

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An Enantioselective Synthetic Route towards Second-Generation Light-Driven Rotary Molecular Motors

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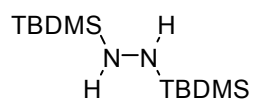
General Experimental

Chemical shifts are denoted in δ -unit (ppm) relative to CDCl_3 (7.26), CD_2Cl_2 (5.30), or toluene- d_8 (2.09) for ^1H NMR and relative to CDCl_3 (77.16), CD_2Cl_2 (53.52), or toluene- d_8 (20.40) for ^{13}C NMR. The splitting parameters for ^1H NMR are denoted as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (double doublet), dt (double triplet), m (multiplet), and b (broad). For ^{13}C NMR, the carbon atoms are assigned as q (primary carbon), t (secondary carbon), d (tertiary carbon), and s (quaternary carbon). Column chromatography was performed on silica gel as described by Still and co-workers.¹ Reactions were performed under a nitrogen atmosphere unless stated otherwise.

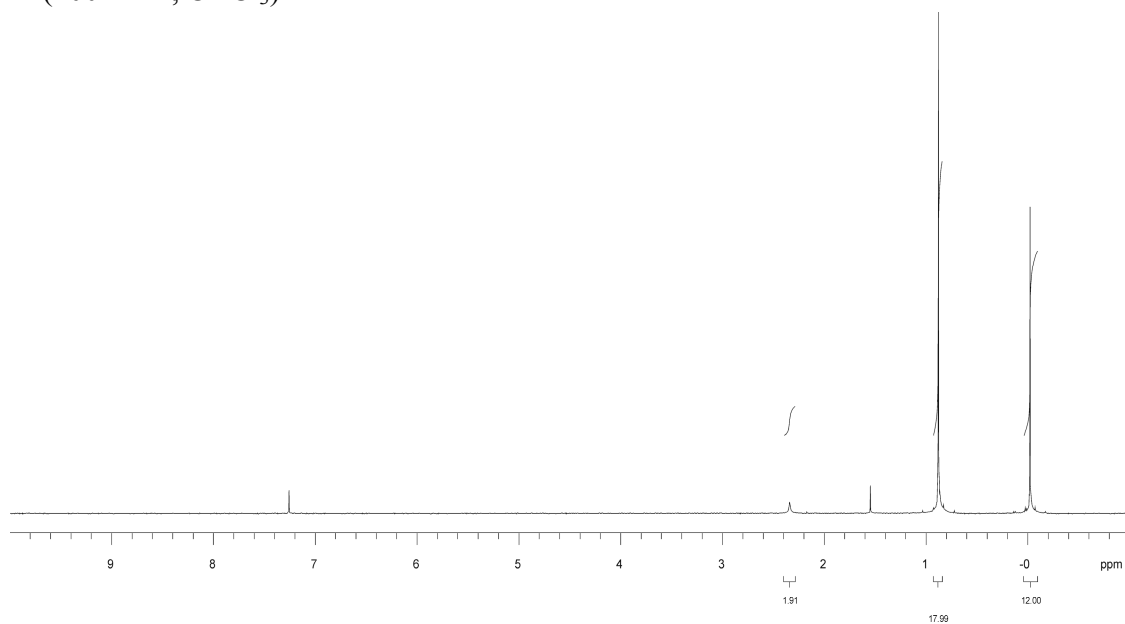
¹ Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.

¹H NMR, ¹³C NMR, and IR Spectra

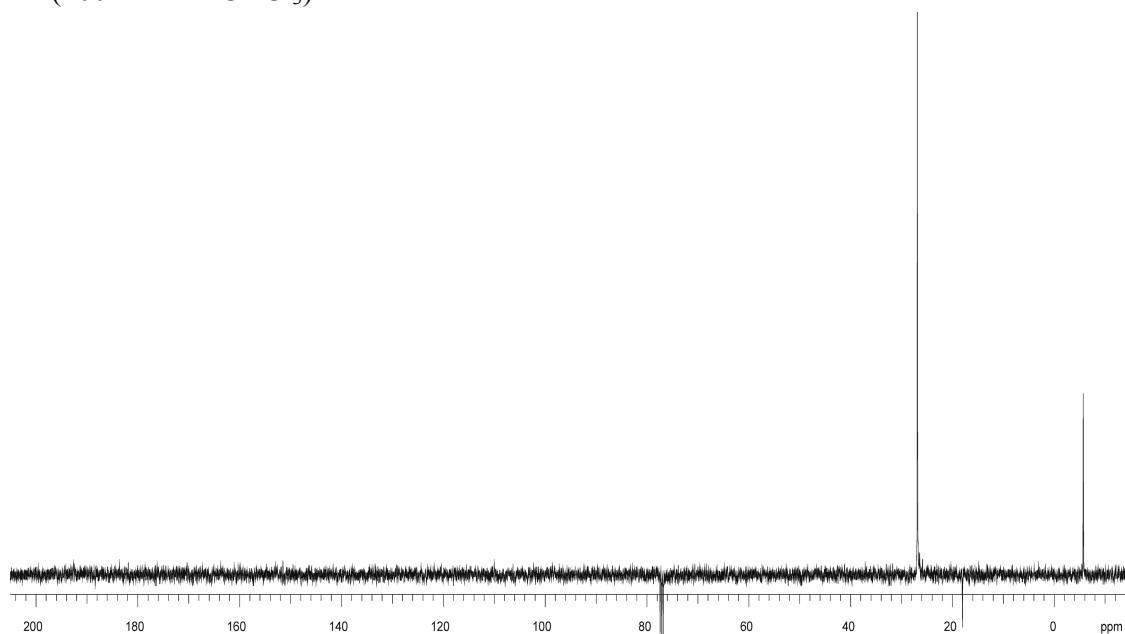
1,2-Bis(*tert*-butyldimethylsilyl)hydrazine



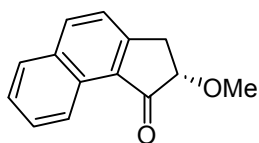
¹H NMR (400 MHz, CDCl₃)



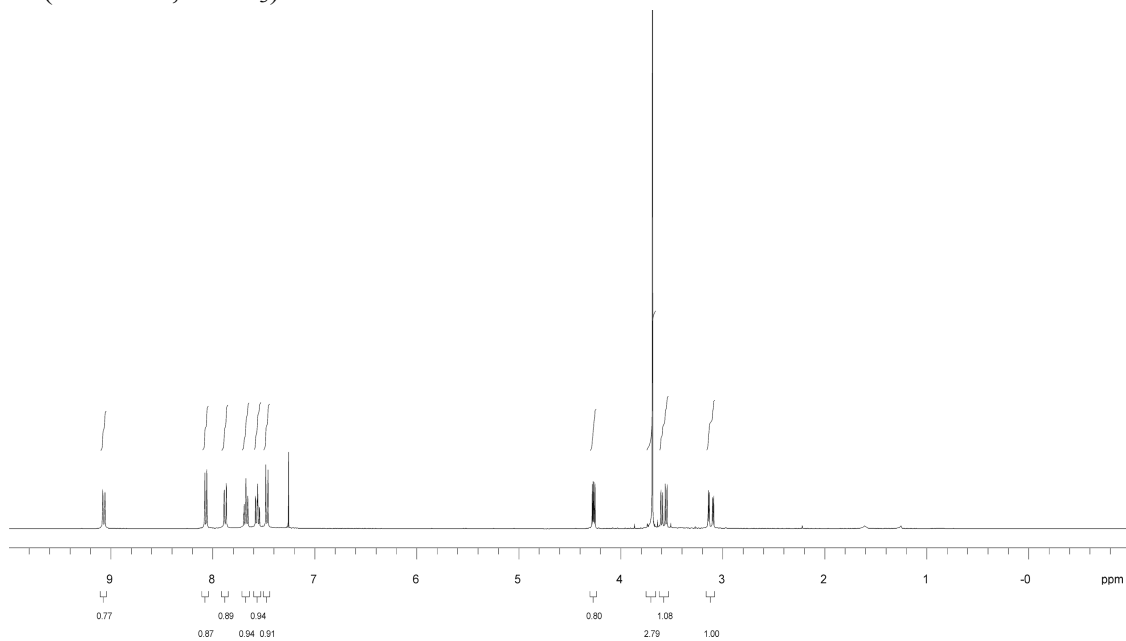
¹³C NMR (100 MHz in CDCl₃)



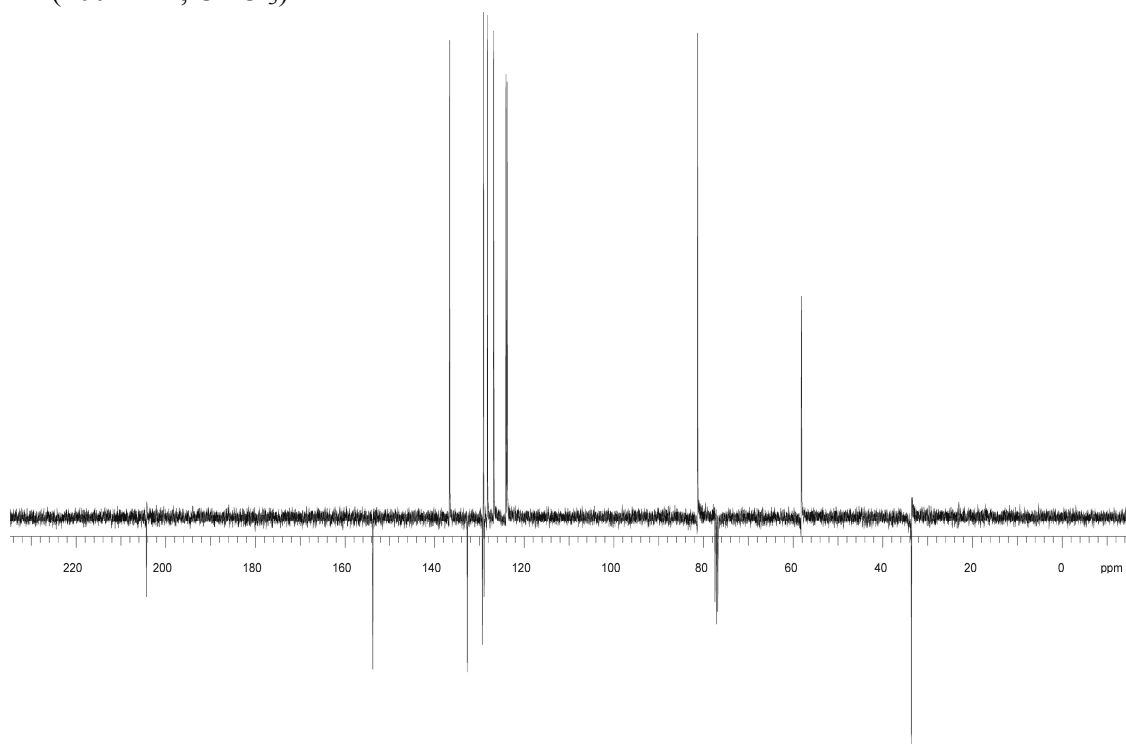
(S)-2-Methoxy-2,3-dihydrocyclopenta[*a*]naphthalen-1-one (4)



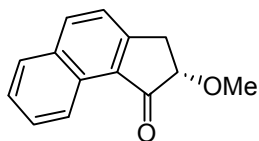
^1H NMR (400 MHz, CDCl_3)



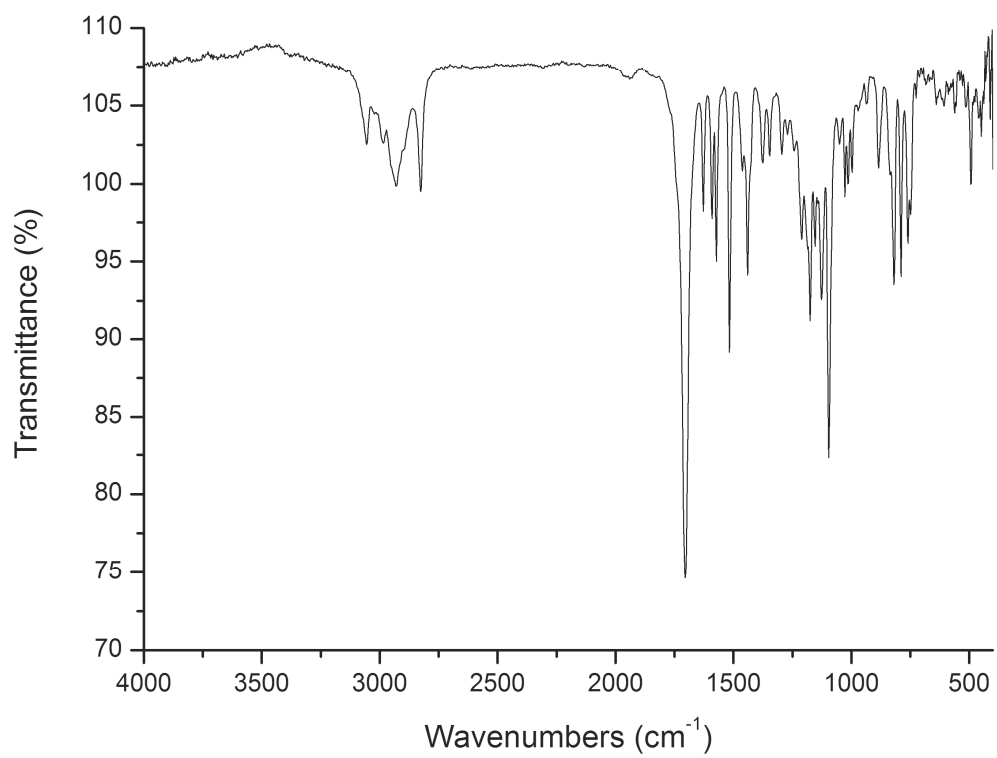
^{13}C NMR (100 MHz, CDCl_3)



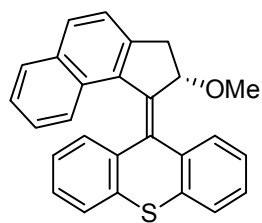
(S)-2-Methoxy-2,3-dihydrocyclopenta[*a*]naphthalen-1-one (4)



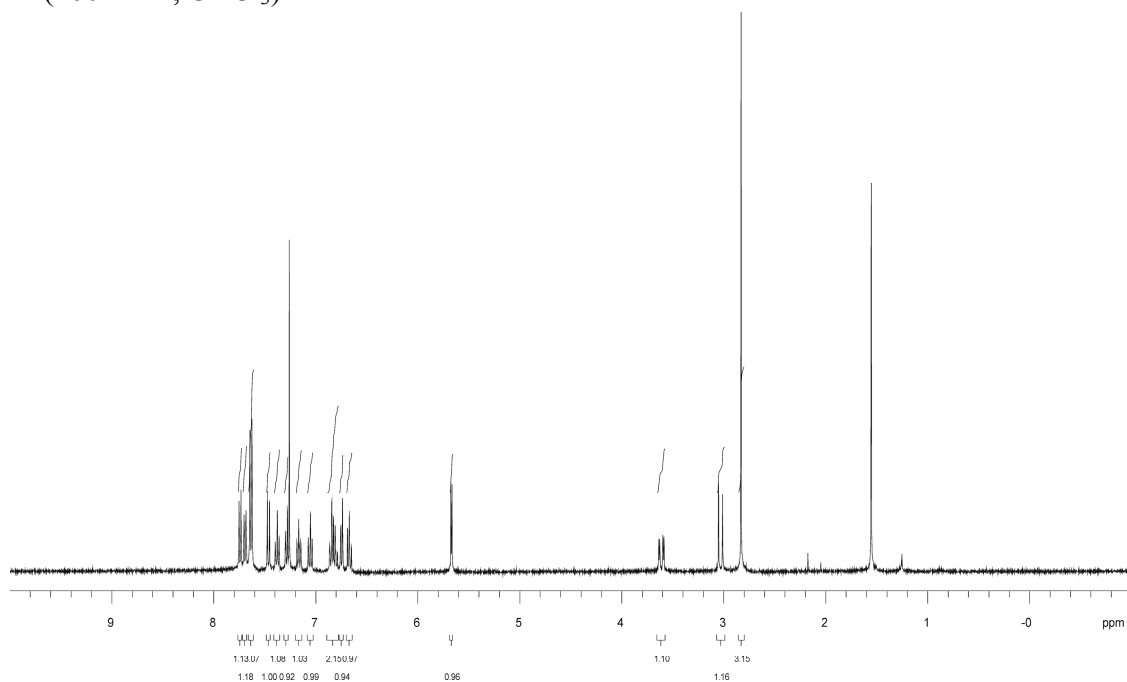
IR (KBr)



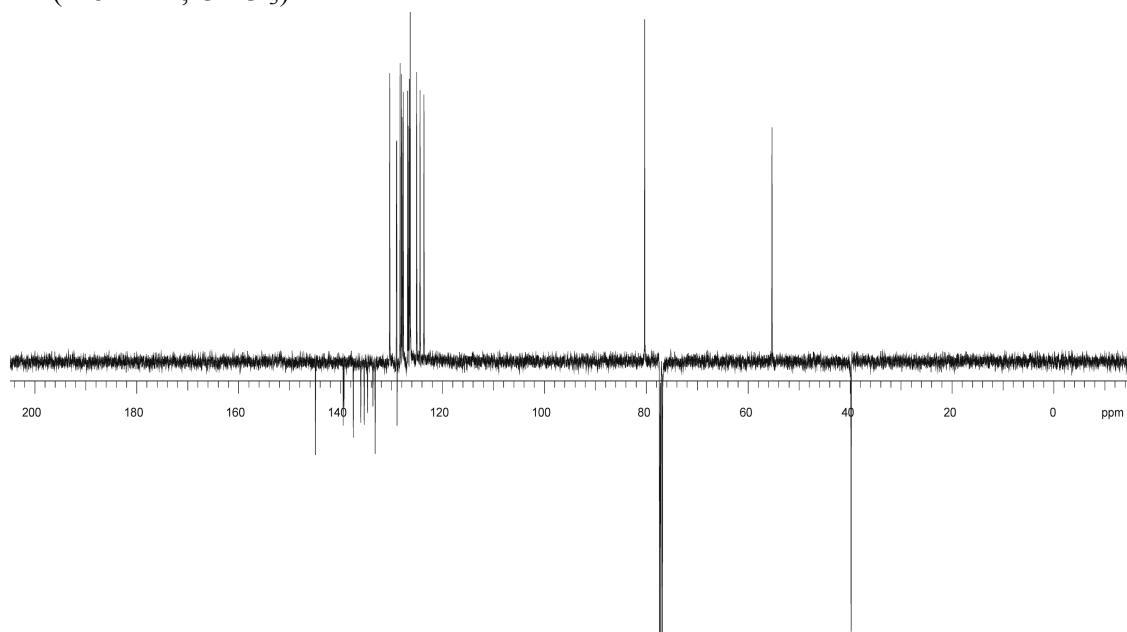
(S)-9-(2'-Methoxy-2',3'-dihydro-1'H-cyclopenta[a]naphthalen-1'-ylidene)-9H-thioxanthene (5)



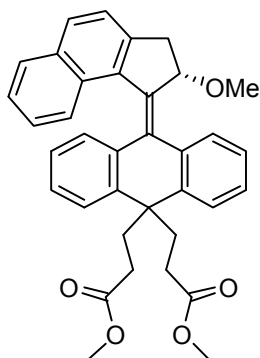
^1H NMR (400 MHz, CDCl_3)



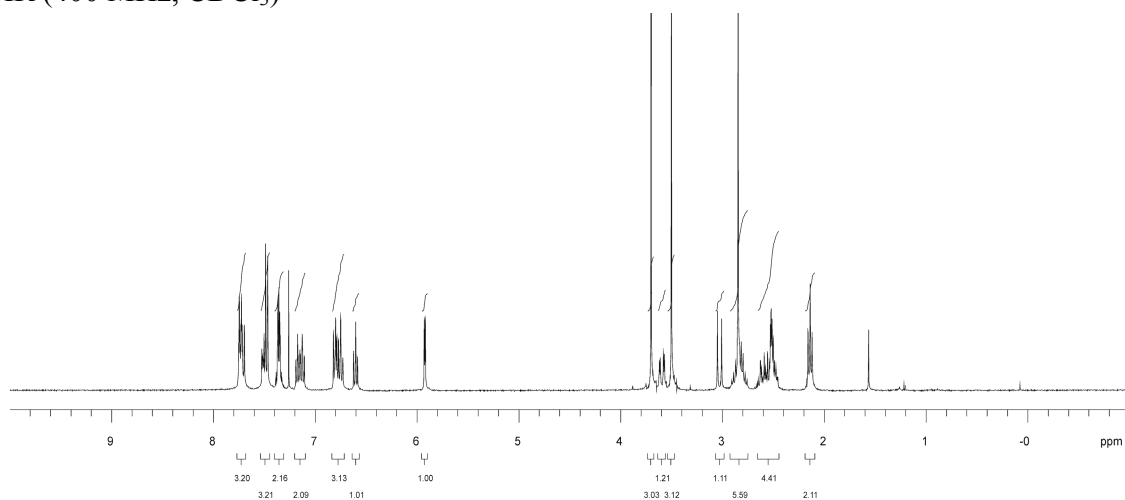
^{13}C NMR (125 MHz, CDCl_3)



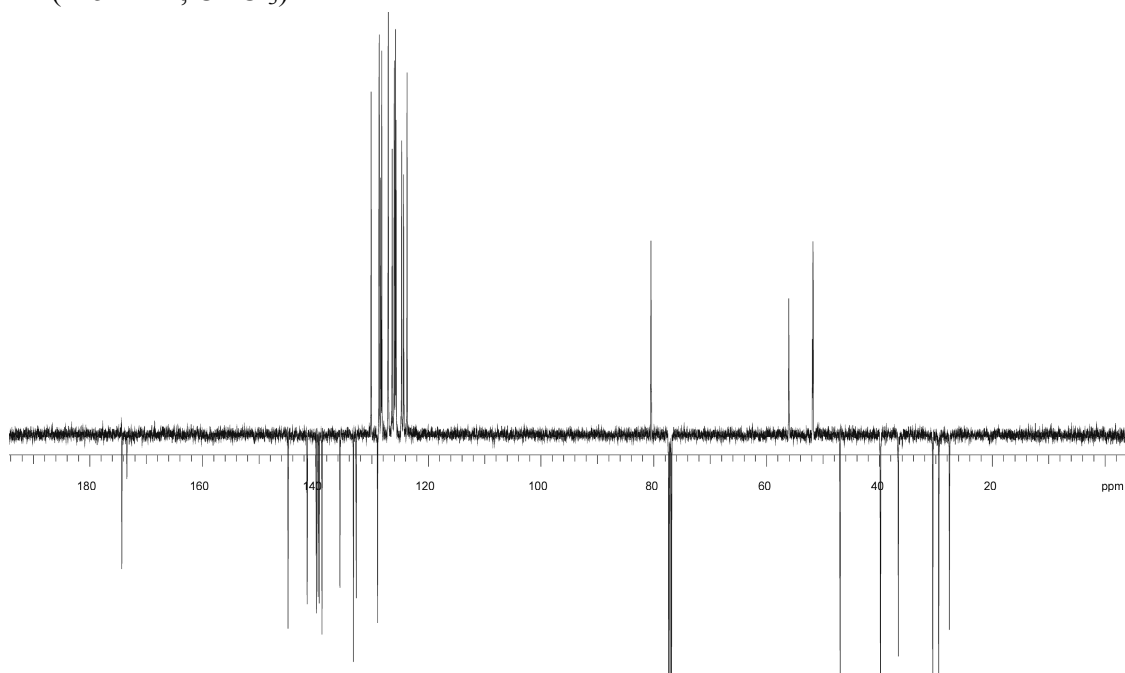
(*S*)-Dimethyl 3,3'-(10-(2'-methoxy-2',3'-dihydro-1'*H*-cyclopenta[*a*]naphthalen-1'-ylidene)-9,10-dihydroanthracene-9,9-diyl)dipropanoate (6)



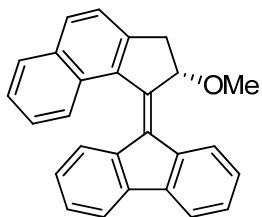
^1H NMR (400 MHz, CDCl_3)



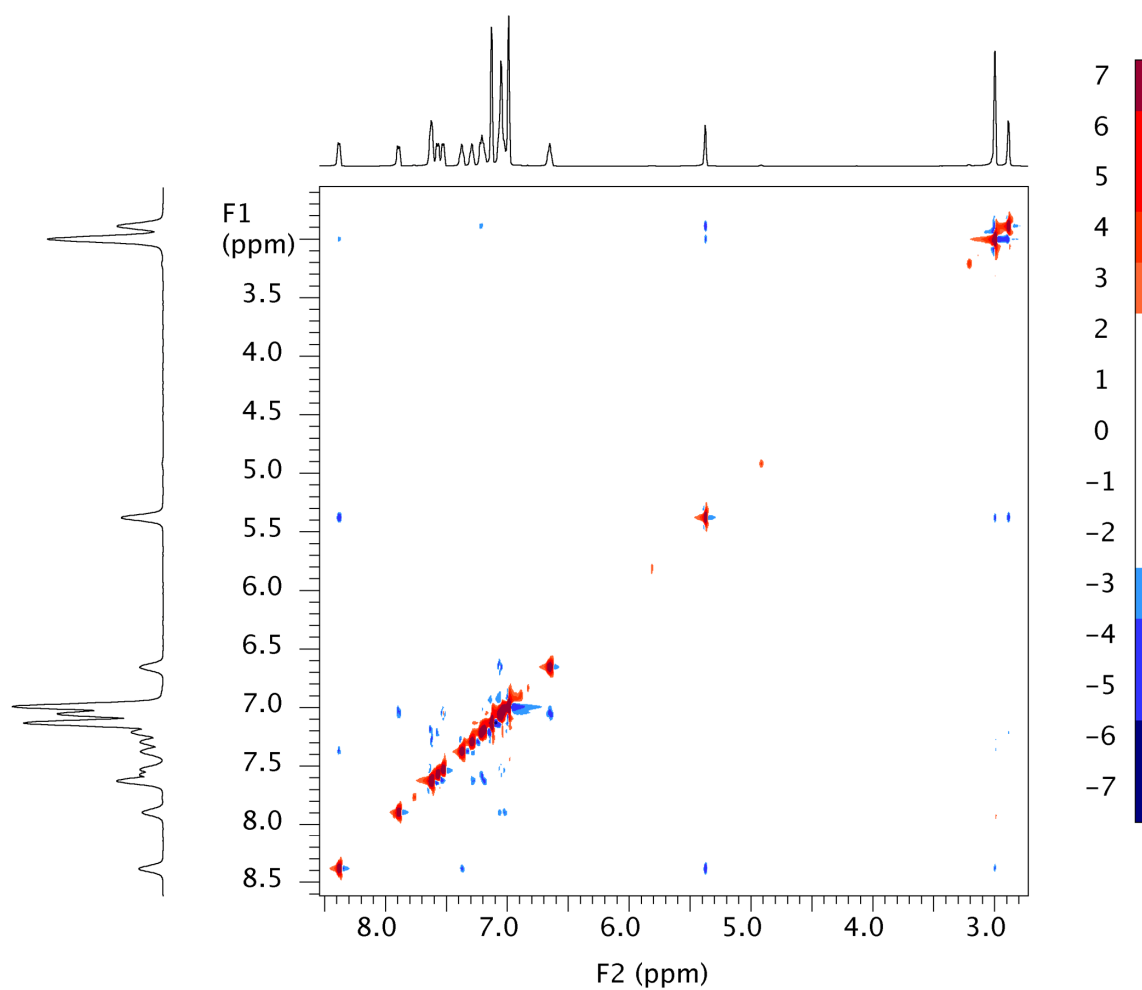
^{13}C NMR (125 MHz, CDCl_3)



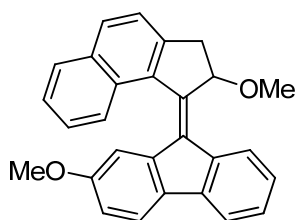
(*S*)-9-(2'-Methoxy-2',3'-dihydro-1'*H*-cyclopenta[*a*]naphthalen-1'-ylidene)-9*H*-fluorene (7)



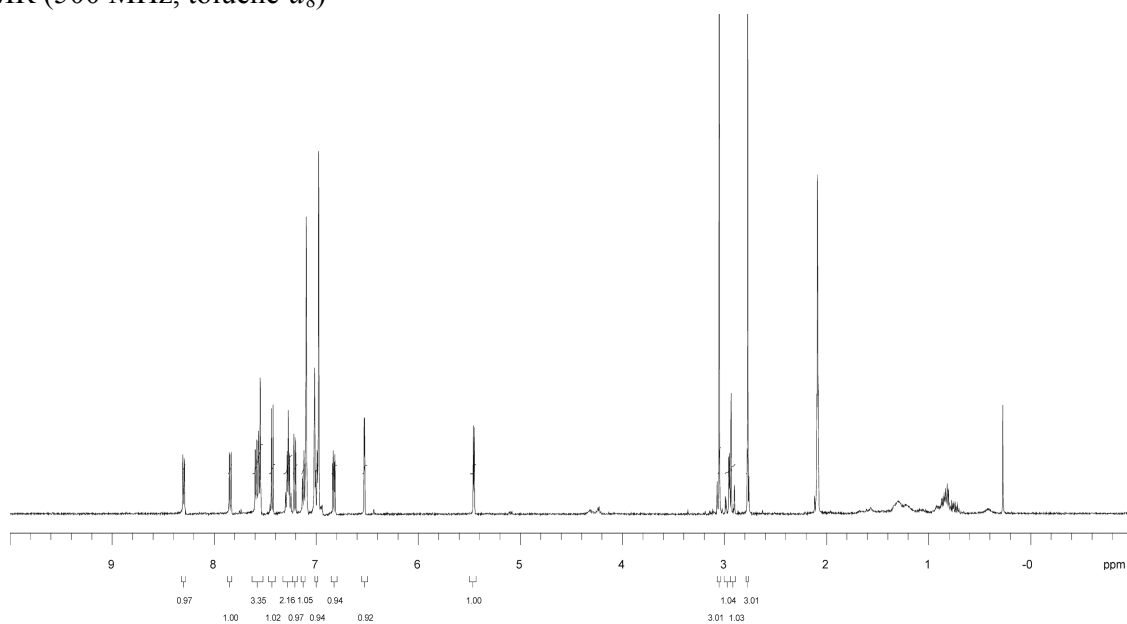
2D NOESY spectrum (500 MHz, toluene-*d*₈, -20 °C)



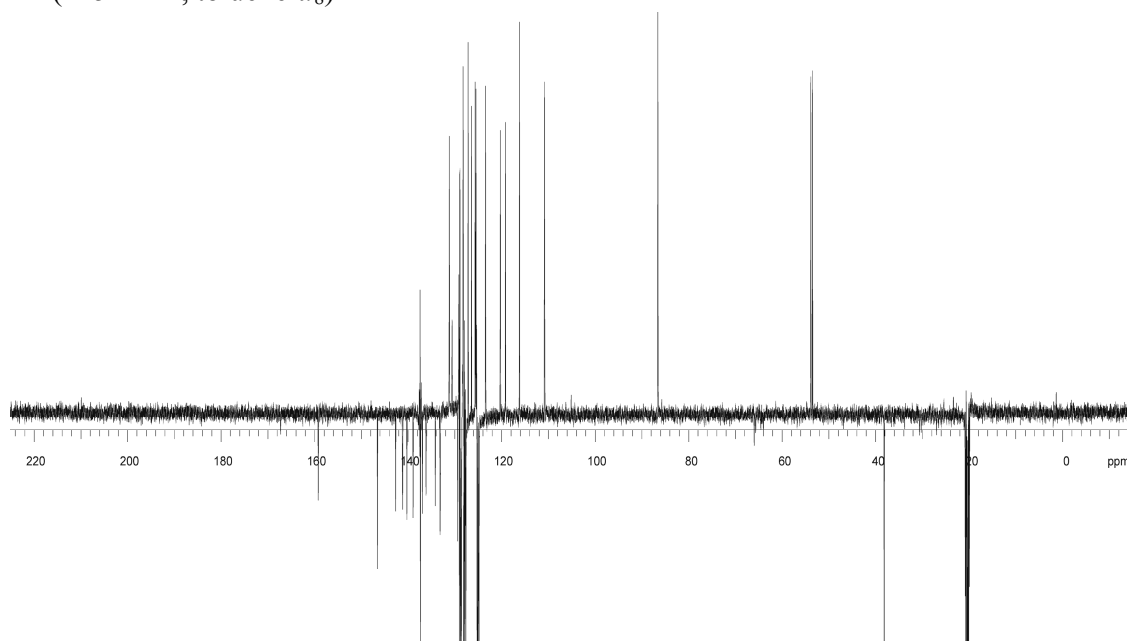
(±)-(E)-2-Methoxy-9-(2'-methoxy-2',3'-dihydro-1'H-cyclopenta[*a*]naphthalen-1'-ylidene)-9H-fluorene (8)



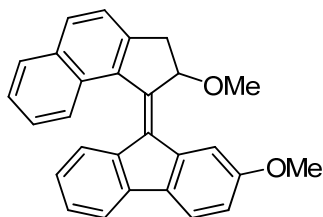
^1H NMR (500 MHz, toluene- d_8)



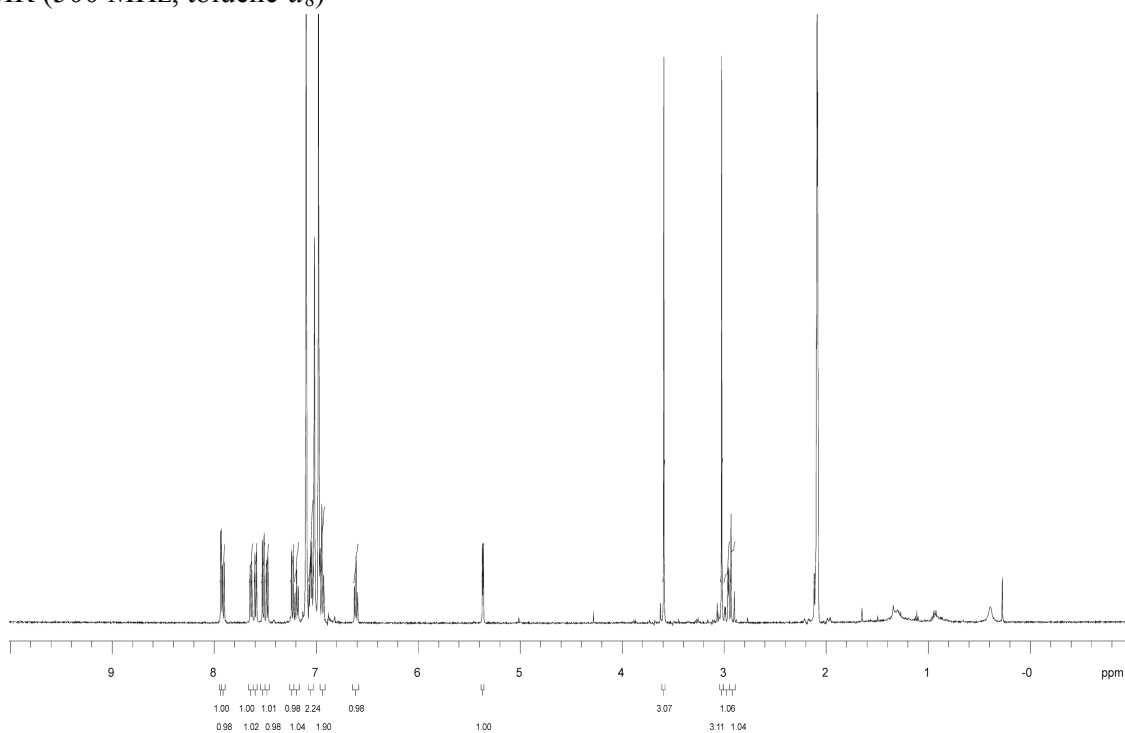
^{13}C NMR (125 MHz, toluene- d_8)



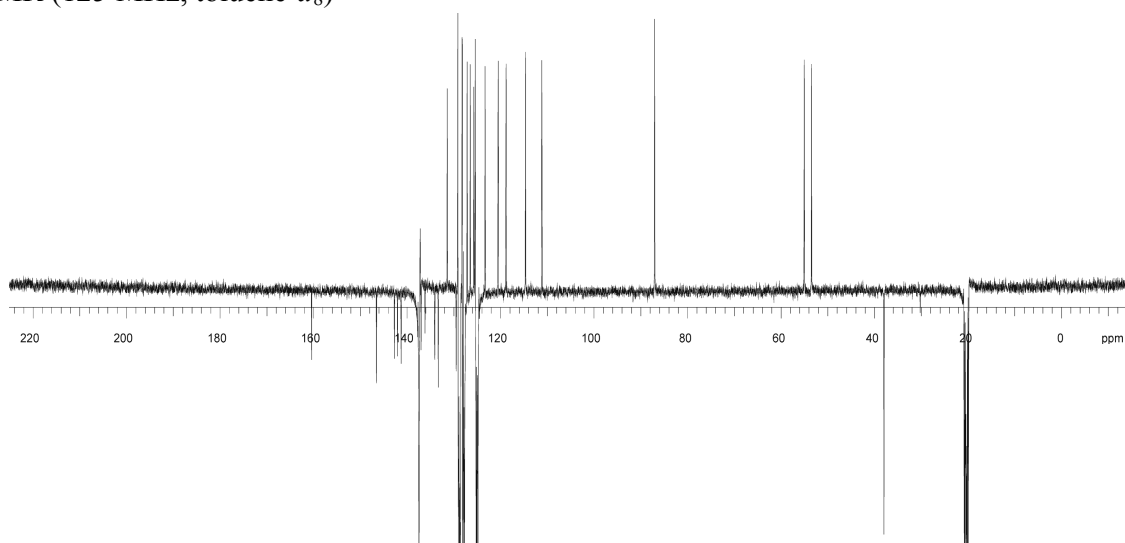
(±)-(Z)-2-Methoxy-9-(2'-methoxy-2',3'-dihydro-1'H-cyclopenta[*a*]naphthalen-1'-ylidene)-9*H*-fluorene (8)



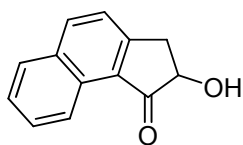
¹H NMR (500 MHz, toluene-*d*₈)



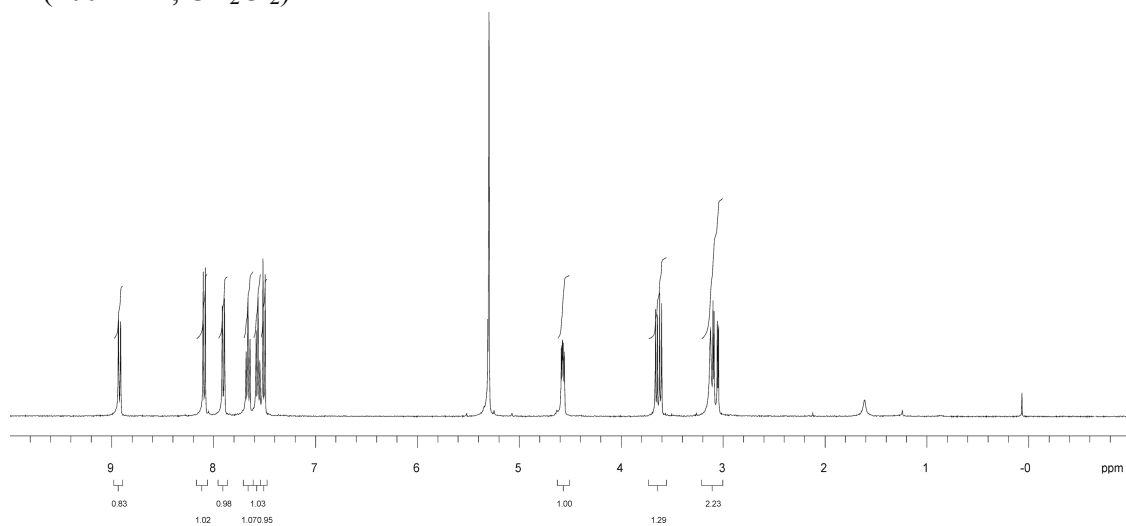
¹³C NMR (125 MHz, toluene-*d*₈)



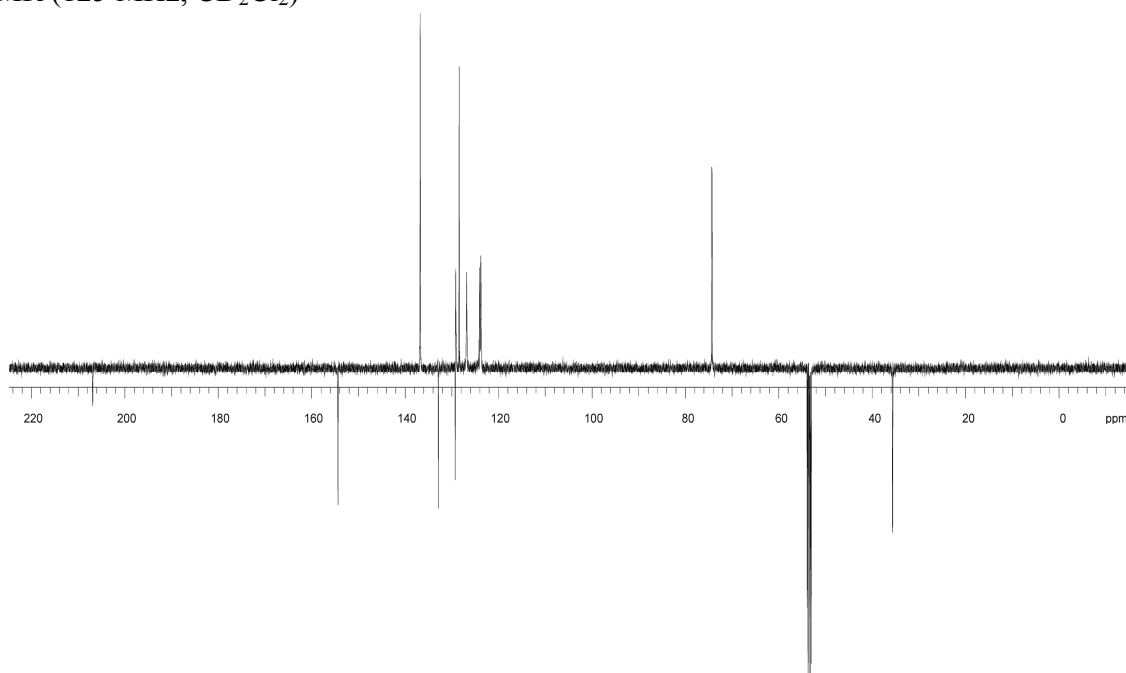
(±)-2-Hydroxy-2,3-dihydrocyclopenta[*a*]naphthalen-1-one (10)



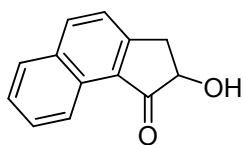
^1H NMR (400 MHz, CD_2Cl_2)



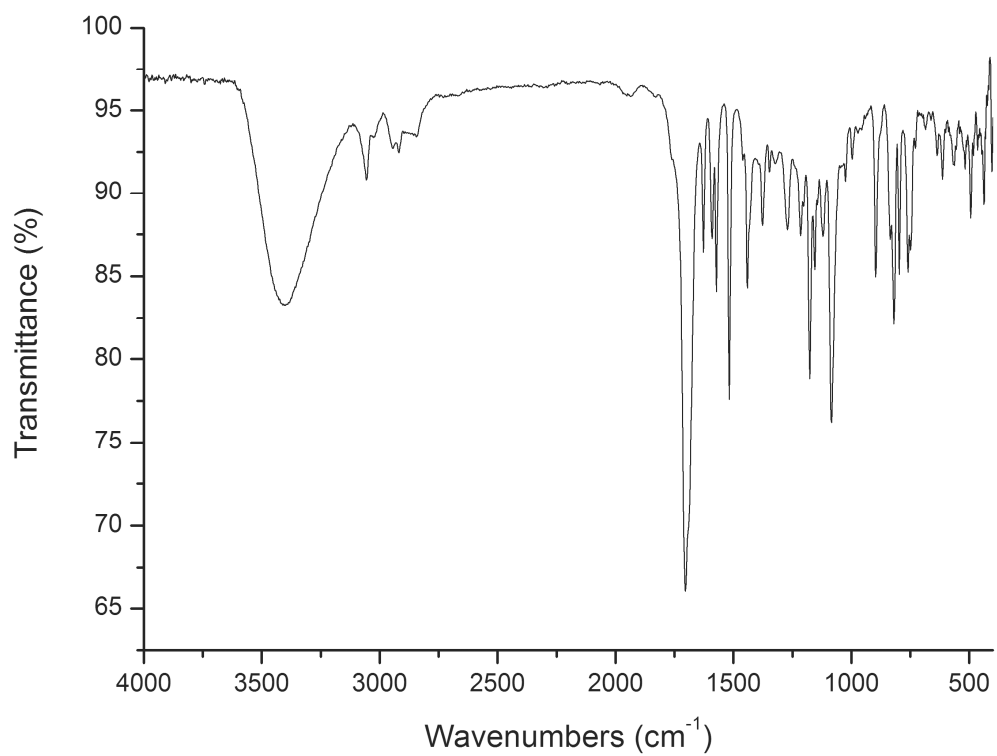
^{13}C NMR (125 MHz, CD_2Cl_2)



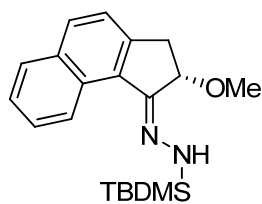
(±)-2-Hydroxy-2,3-dihydrocyclopenta[*a*]naphthalen-1-one (10)



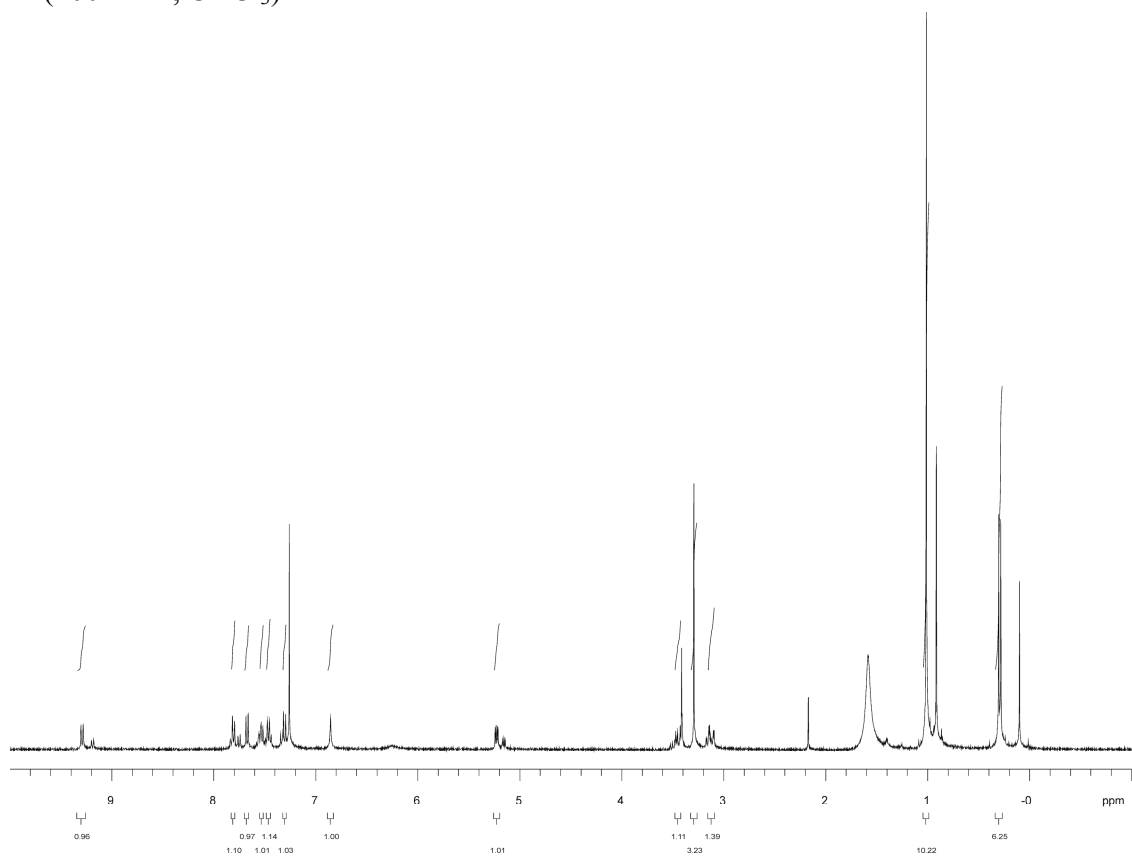
IR (KBr)



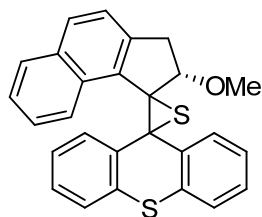
(S)-1-(*tert*-Butyldimethylsilyl)-2-(2-methoxy-2,3-dihydrocyclopenta[*a*]naphthalen-1-ylidene)hydrazine (11)



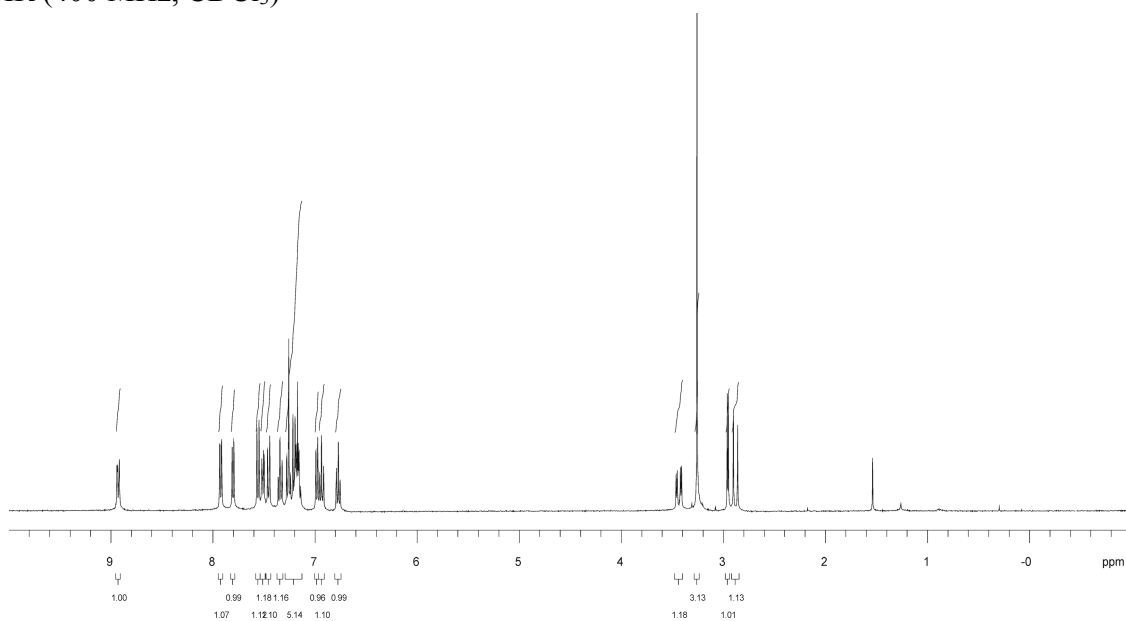
^1H NMR (400 MHz, CDCl_3)



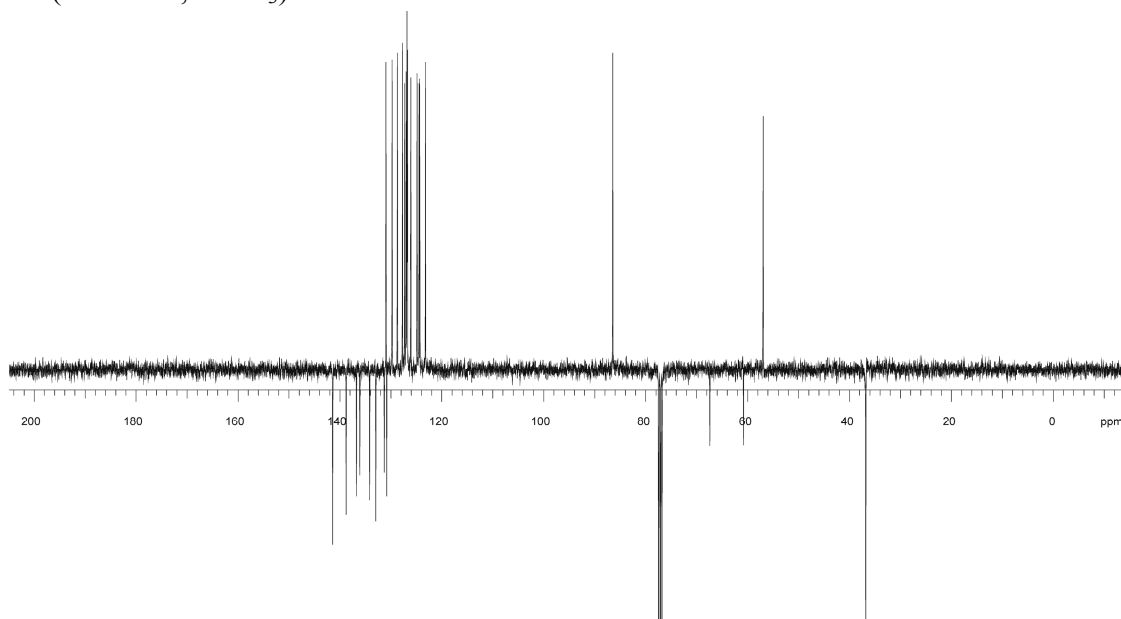
(*S*)-Dispiro[2-methoxy-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene-1,2'-thiirane-3',9''-thioxanthene] (13)



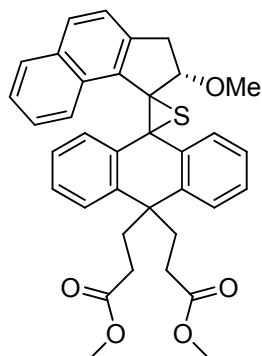
^1H NMR (400 MHz, CDCl_3)



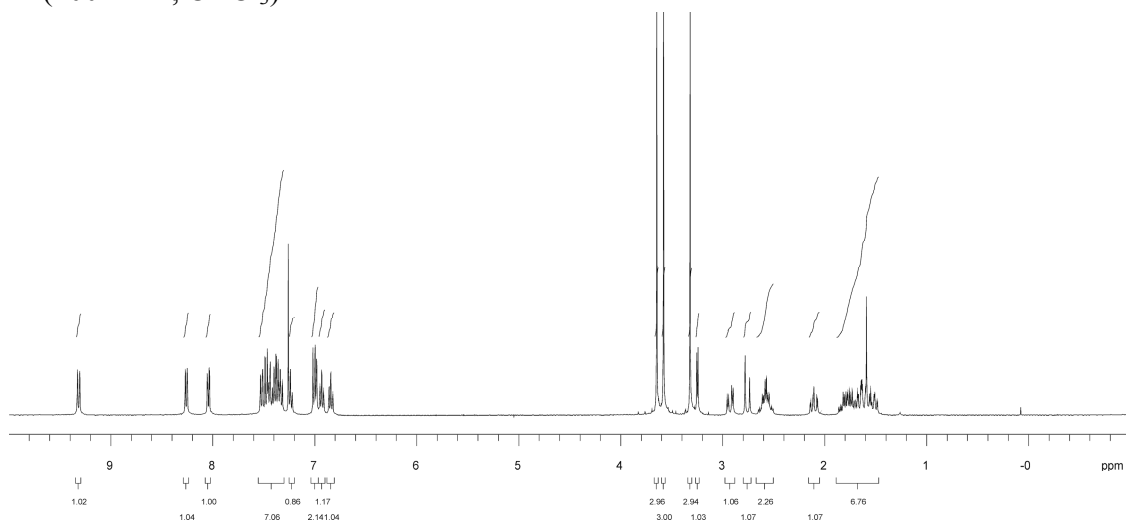
^{13}C NMR (100 MHz, CDCl_3)



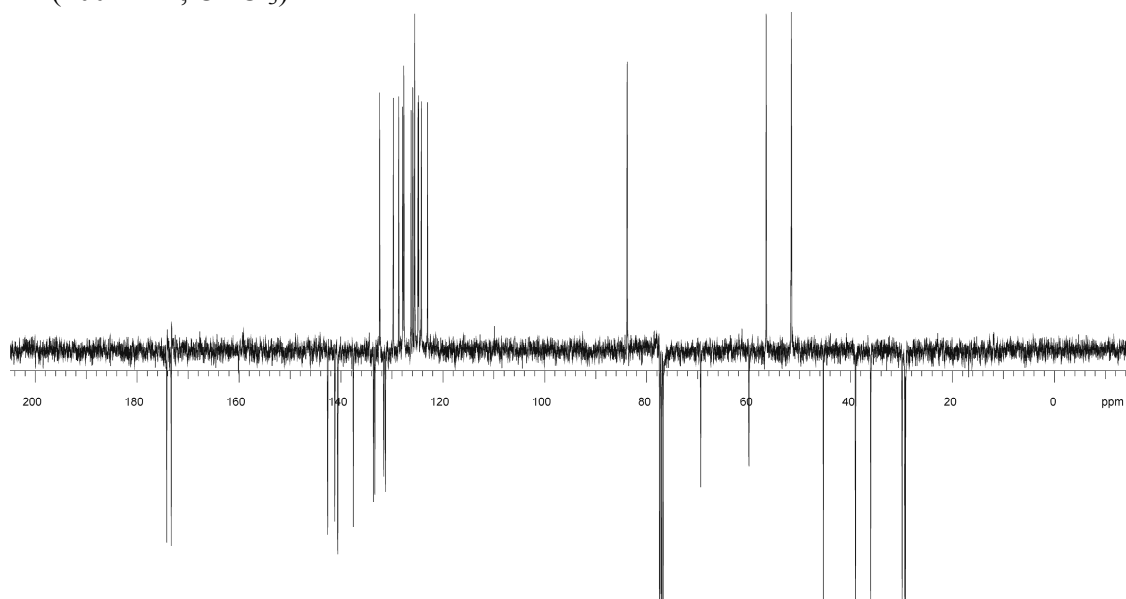
(S)-Dispiro[dimethyl 3,3'-(2-methoxy-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1,2'-thiirane-3',9''-(9'',10''-dihydroanthracene-9'',9''-diyl)dipropanoate)] (15)



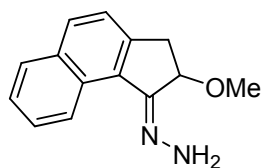
^1H NMR (400 MHz, CDCl_3)



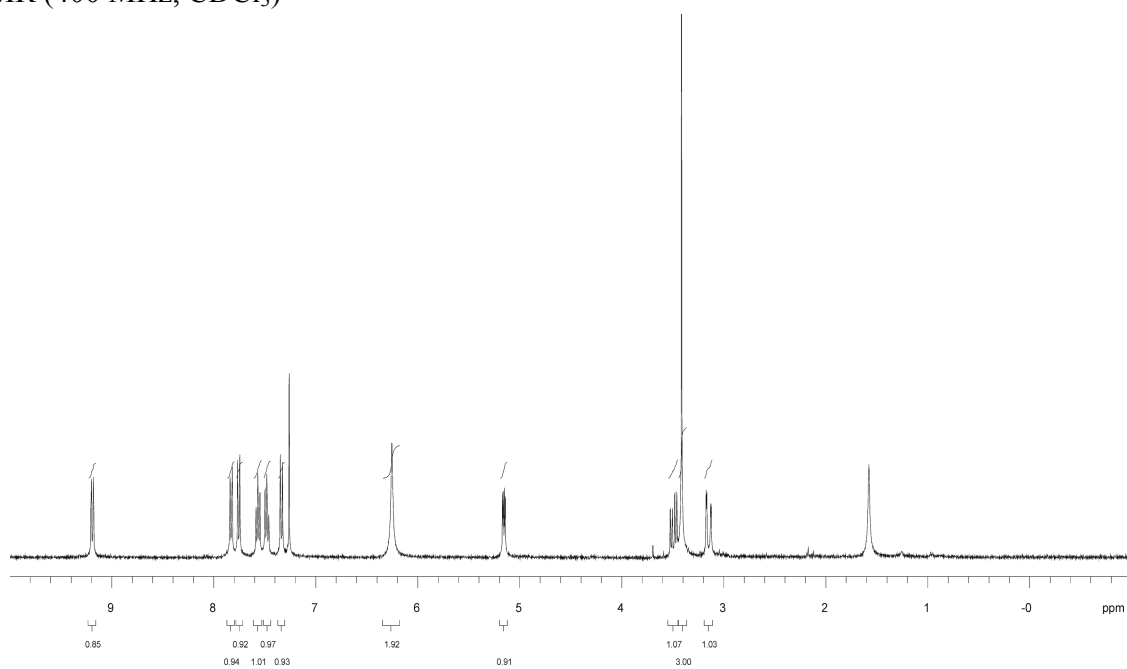
^{13}C NMR (100 MHz, CDCl_3)



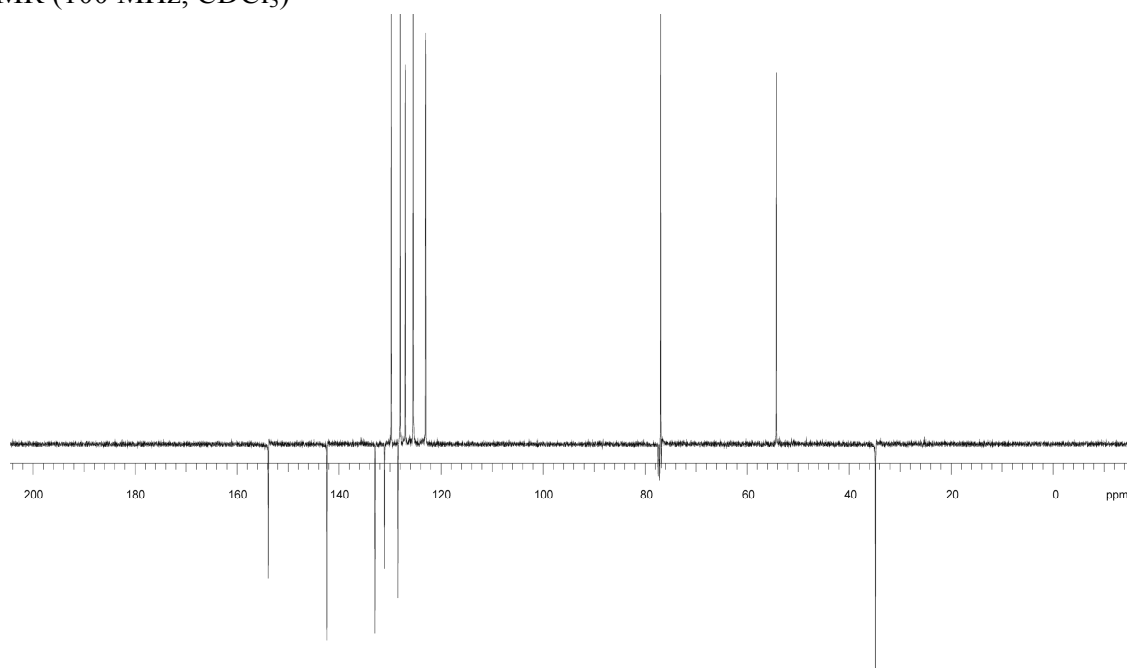
(±)-(2-Methoxy-2,3-dihydrocyclopenta[*a*]naphthalen-1-ylidene)hydrazine (18)



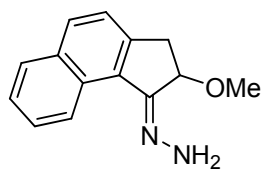
^1H NMR (400 MHz, CDCl_3)



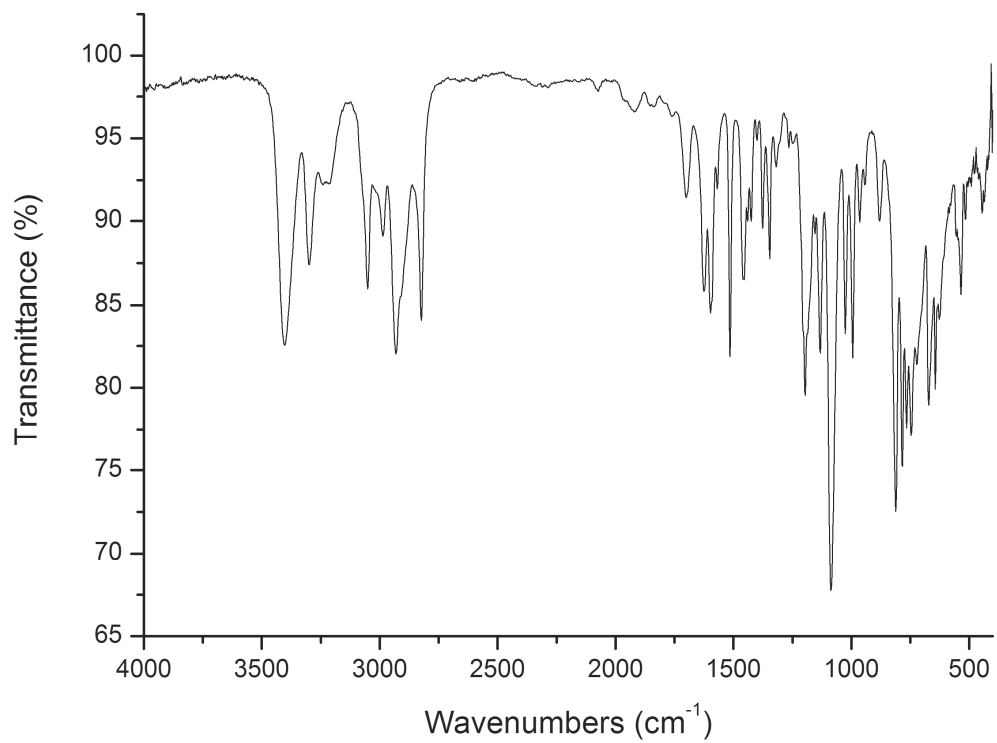
^{13}C NMR (100 MHz, CDCl_3)



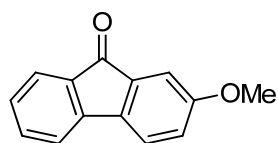
(±)-(2-Methoxy-2,3-dihydrocyclopenta[*a*]naphthalen-1-ylidene)hydrazine (18)



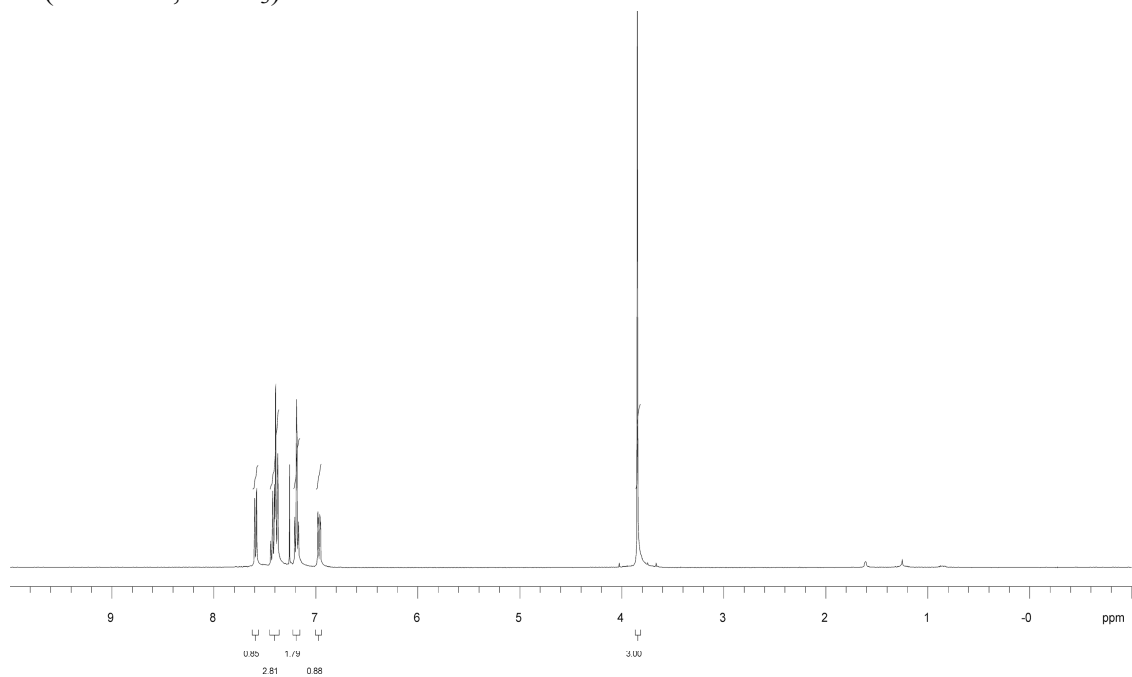
IR (KBr)



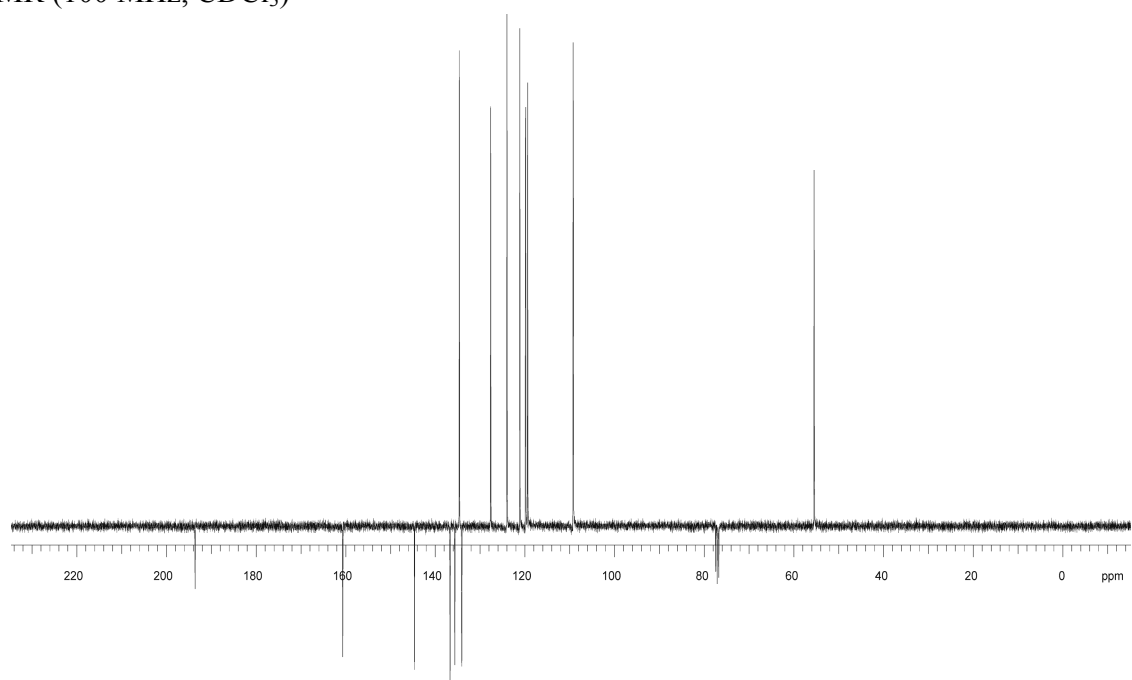
2-Methoxyfluoren-9-one (19)



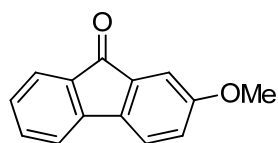
^1H NMR (400 MHz, CDCl_3)



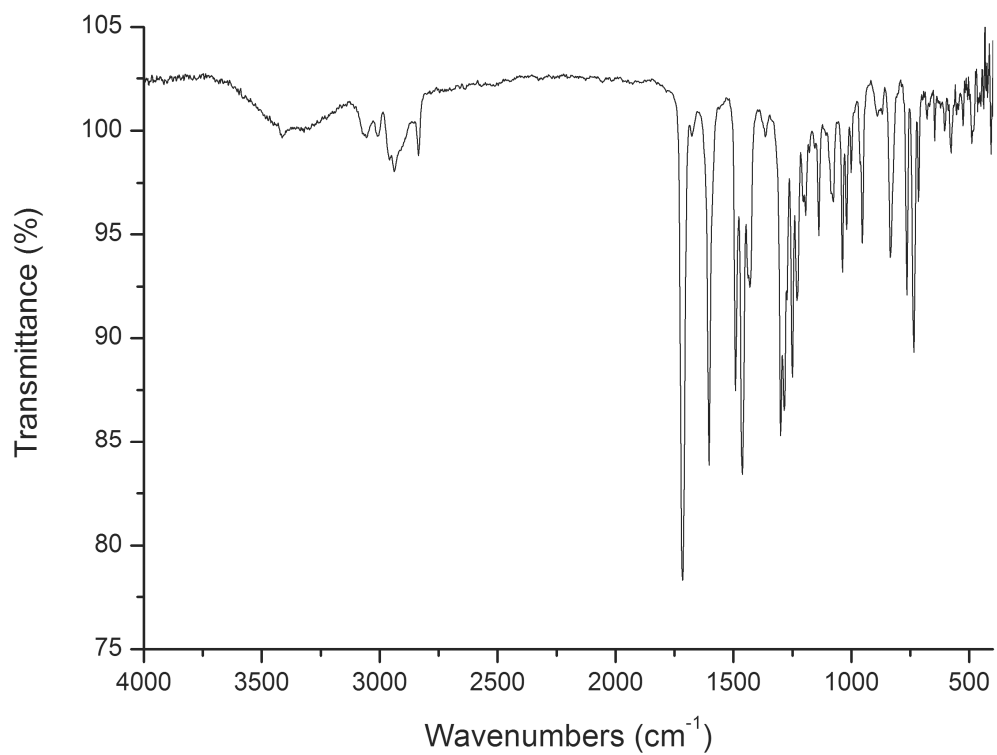
^{13}C NMR (100 MHz, CDCl_3)



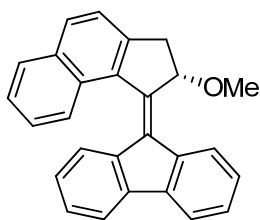
2-Methoxyfluoren-9-one (19)



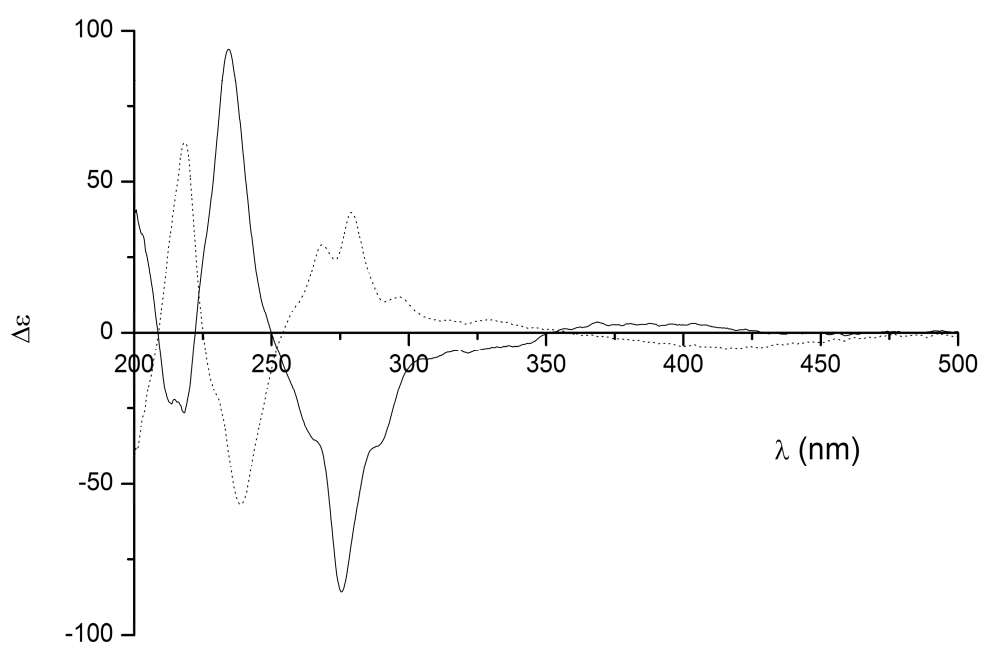
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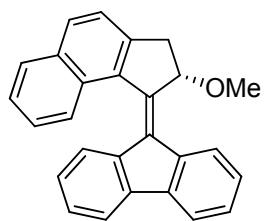


CD, UV/Vis, and ^1H NMR Spectra of Irradiation Experiments

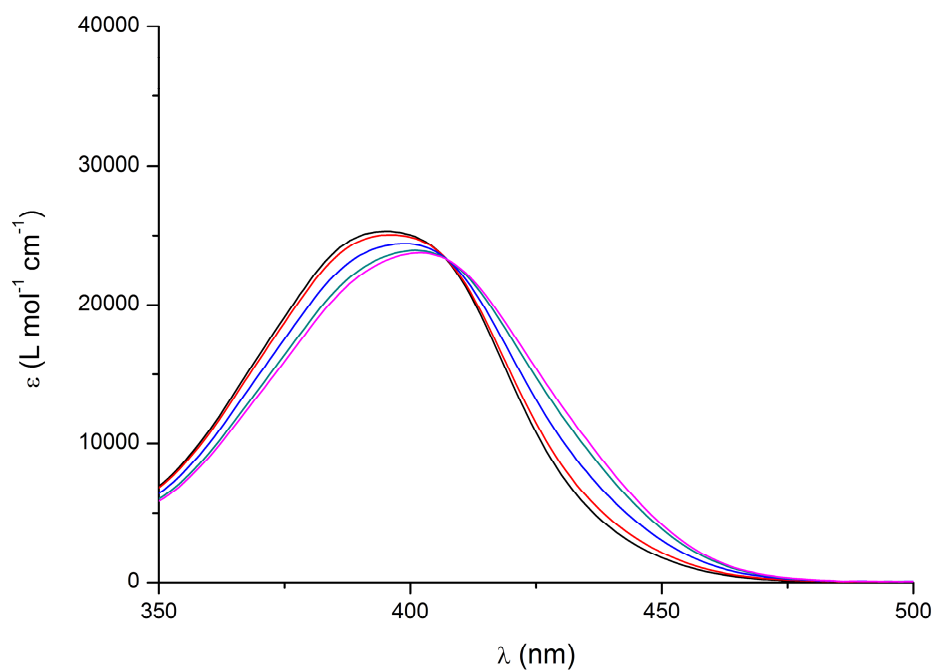
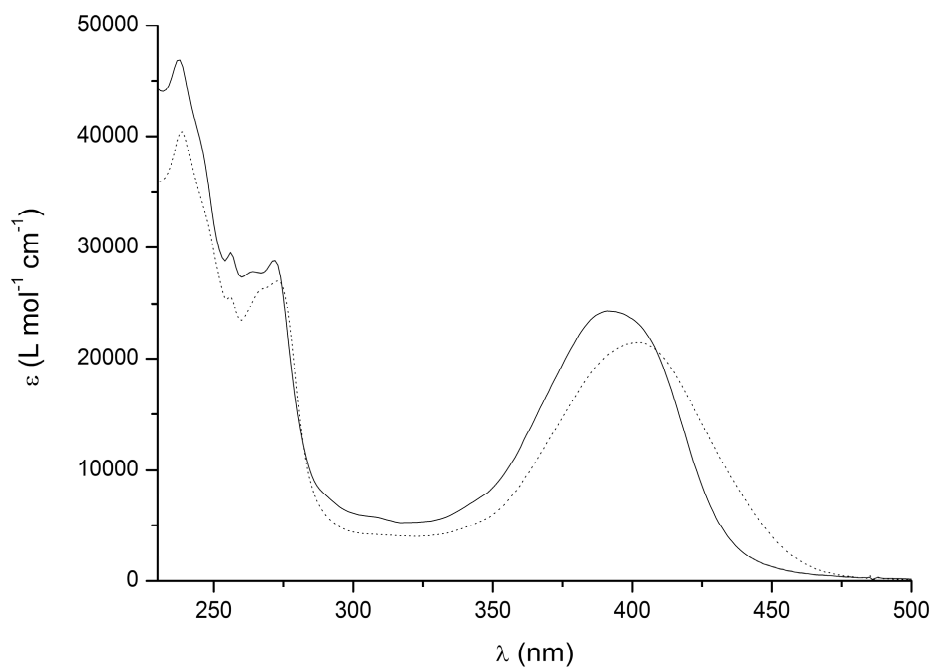


CD spectra of alkene (*S*)-7 in *n*-hexane at $-10\text{ }^\circ\text{C}$ before (solid) and after (dashed) irradiation at 365 nm.

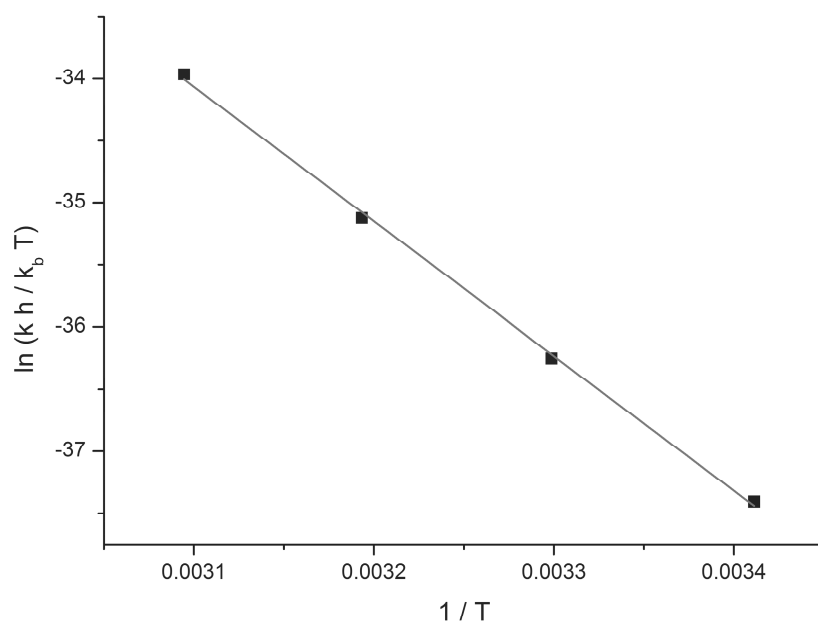


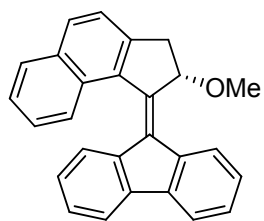


UV/Vis spectra of alkene (*S*)-**7** in *n*-hexane at $-20\text{ }^{\circ}\text{C}$ before (solid) and after (dashed) irradiation at 365 nm.

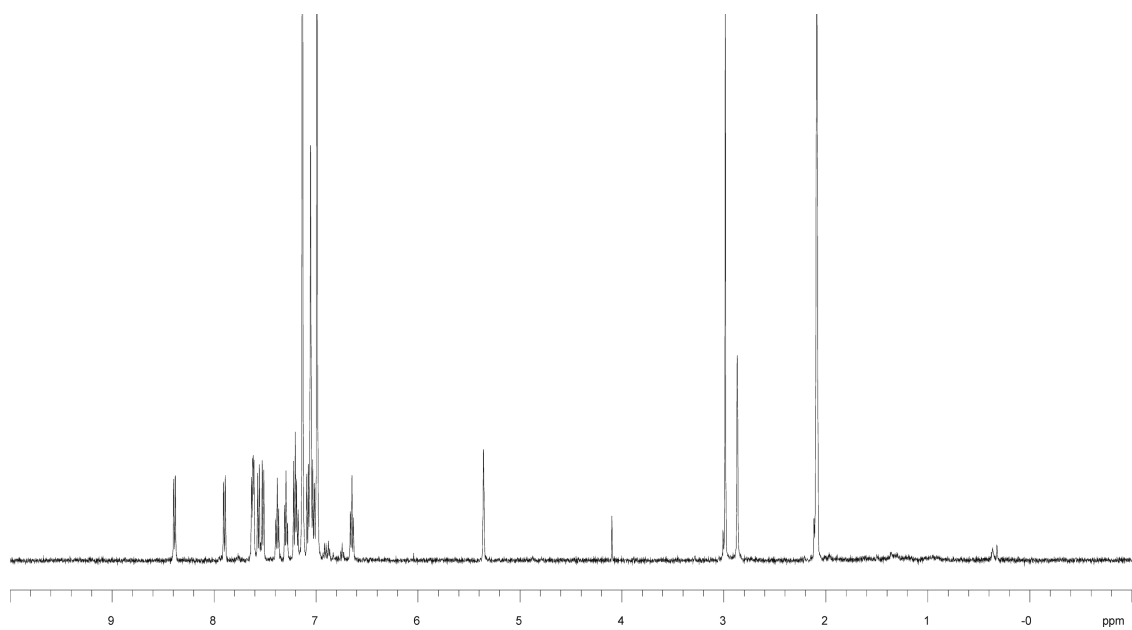


The Eyring Plot used for the determination of the kinetic parameters of the thermal helix inversion of (S)-7:

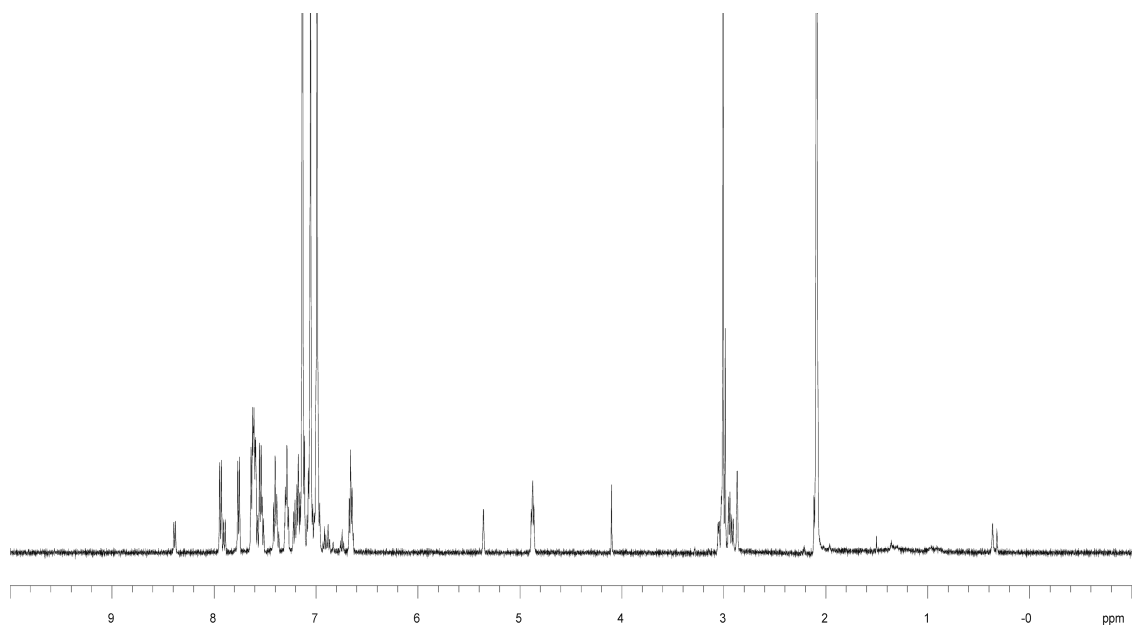




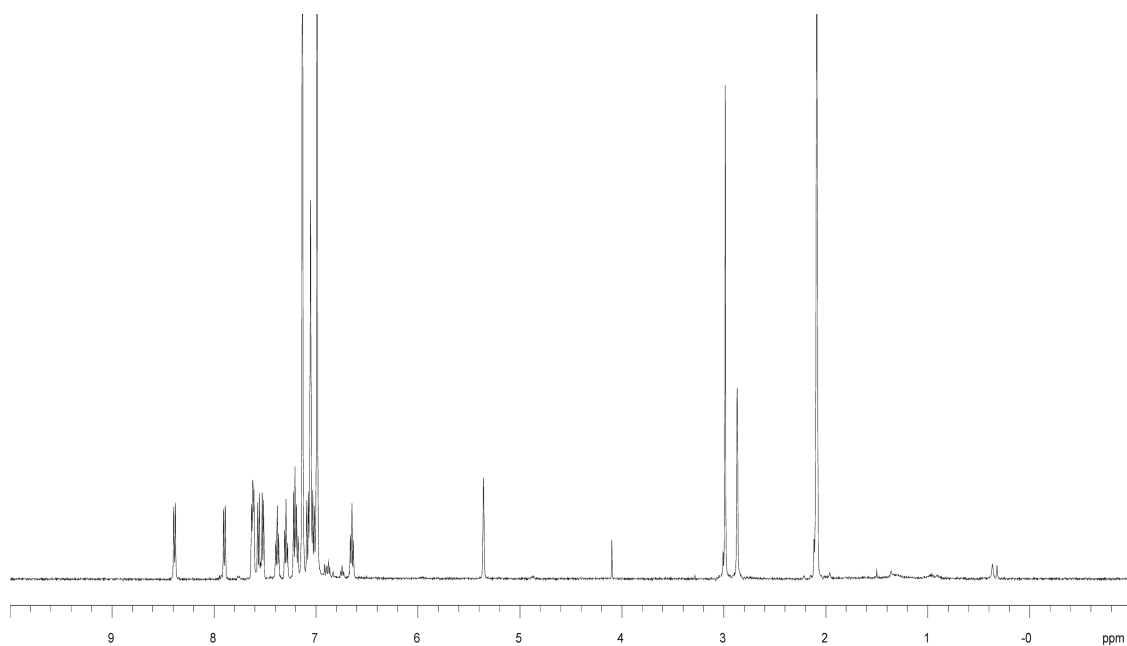
¹H NMR spectrum (500 MHz, toluene-*d*₈, −30 °C) of (*S*)-**7** before irradiation:

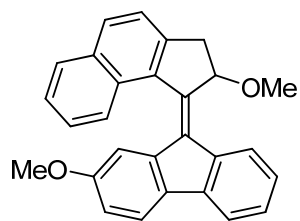


¹H NMR spectrum (500 MHz, toluene-*d*₈, −30 °C) of (*S*)-**7** after irradiation:

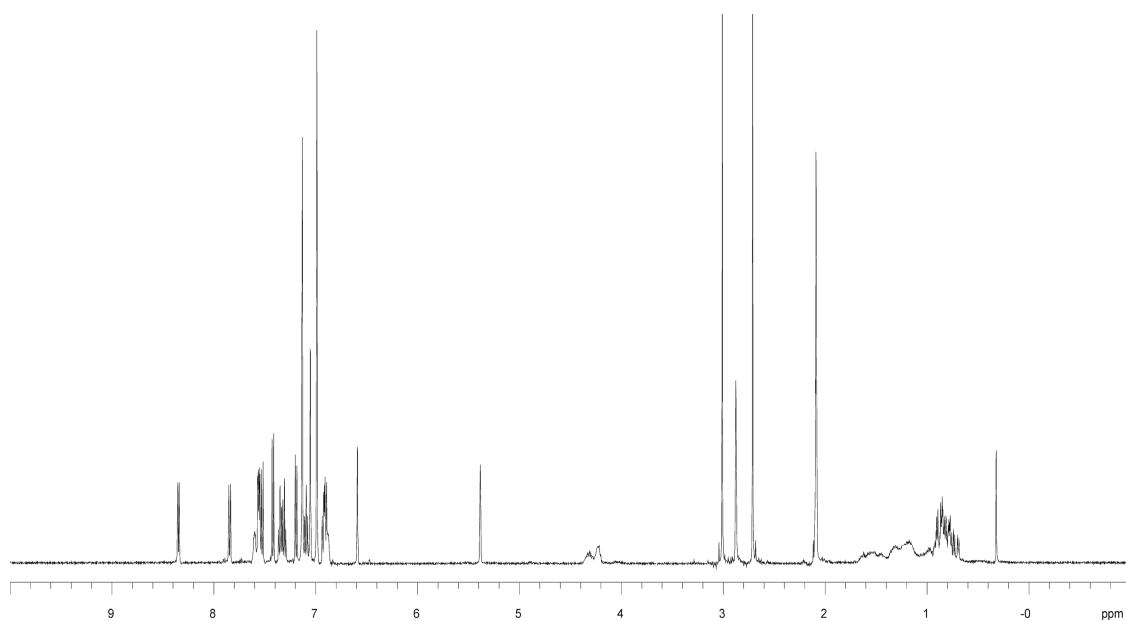


^1H NMR spectrum (500 MHz, toluene- d_8 , $-30\text{ }^\circ\text{C}$) of (*S*)-**7** after subsequent heating:

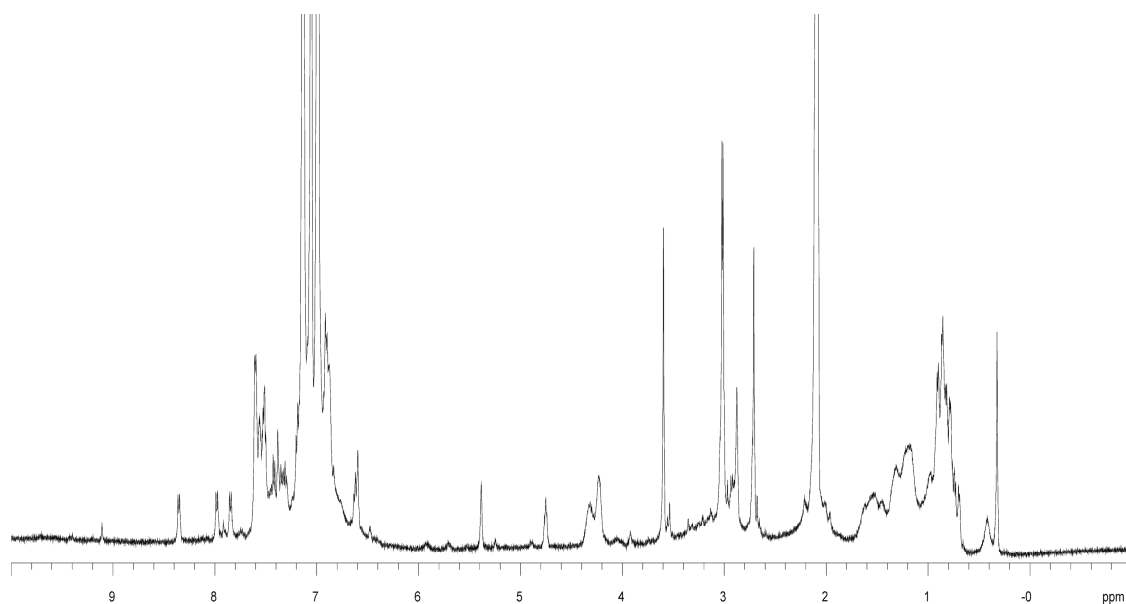




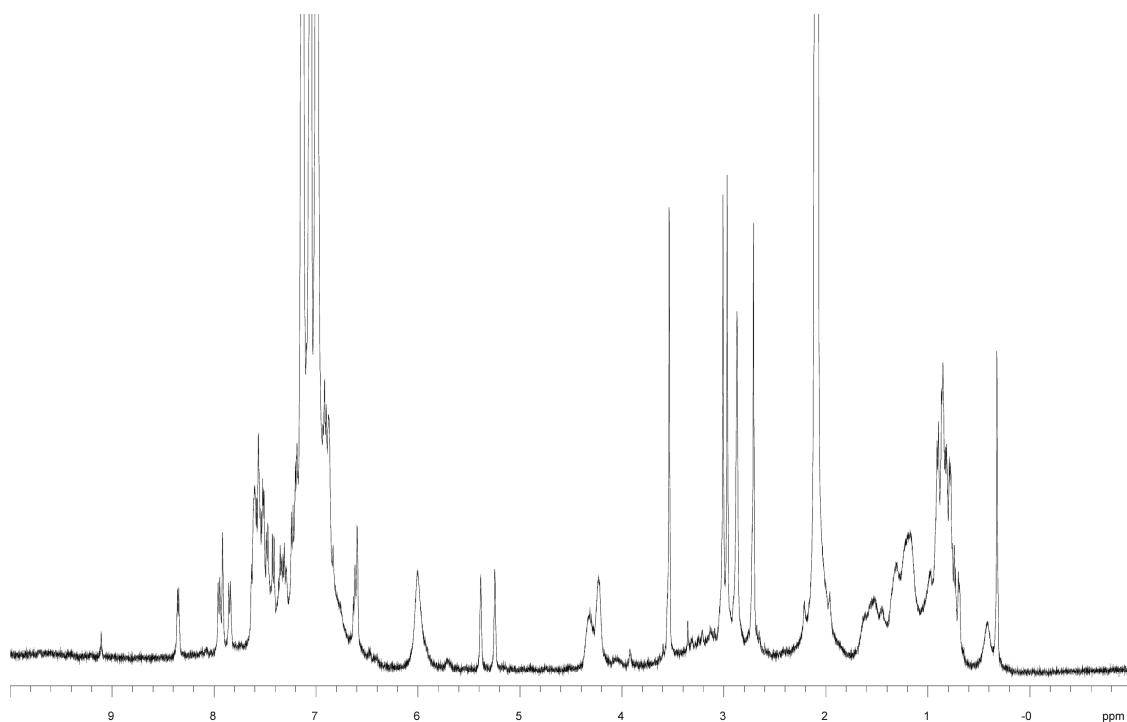
^1H NMR spectrum (500 MHz, toluene- d_8 , $-30\text{ }^\circ\text{C}$) of (*E*)-**8** before irradiation:

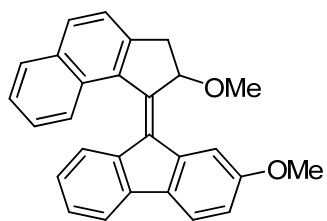


^1H NMR spectrum (500 MHz, toluene- d_8 , $-30\text{ }^\circ\text{C}$) of (*E*)-**8** after irradiation:

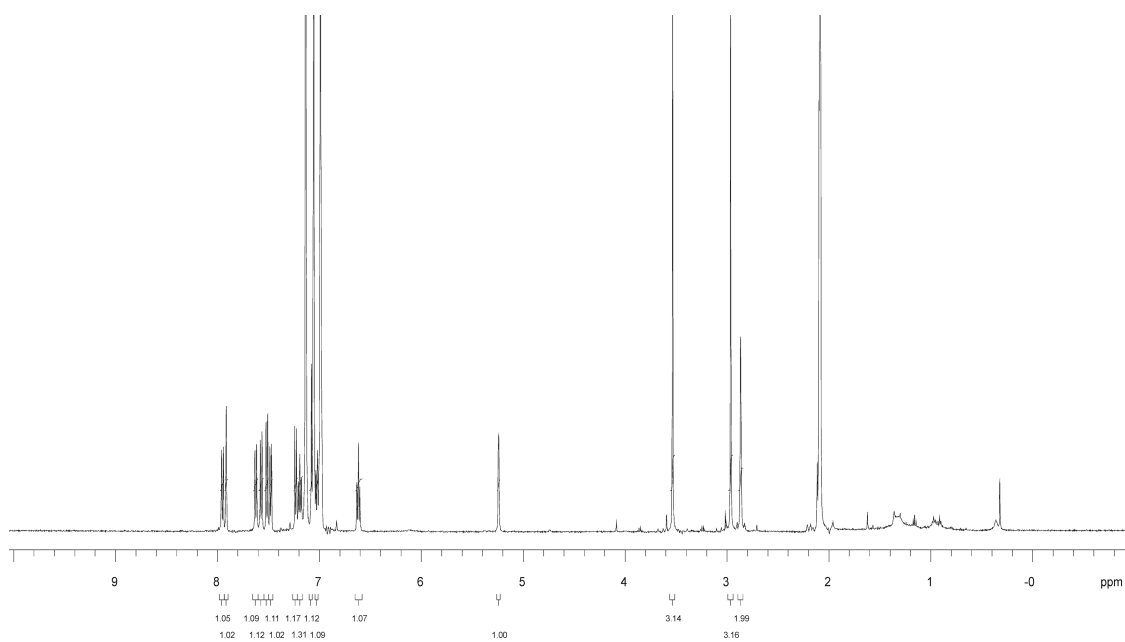


^1H NMR spectrum (500 MHz, toluene- d_8 , $-30\text{ }^\circ\text{C}$) of (*E*)-**8** after subsequent heating:

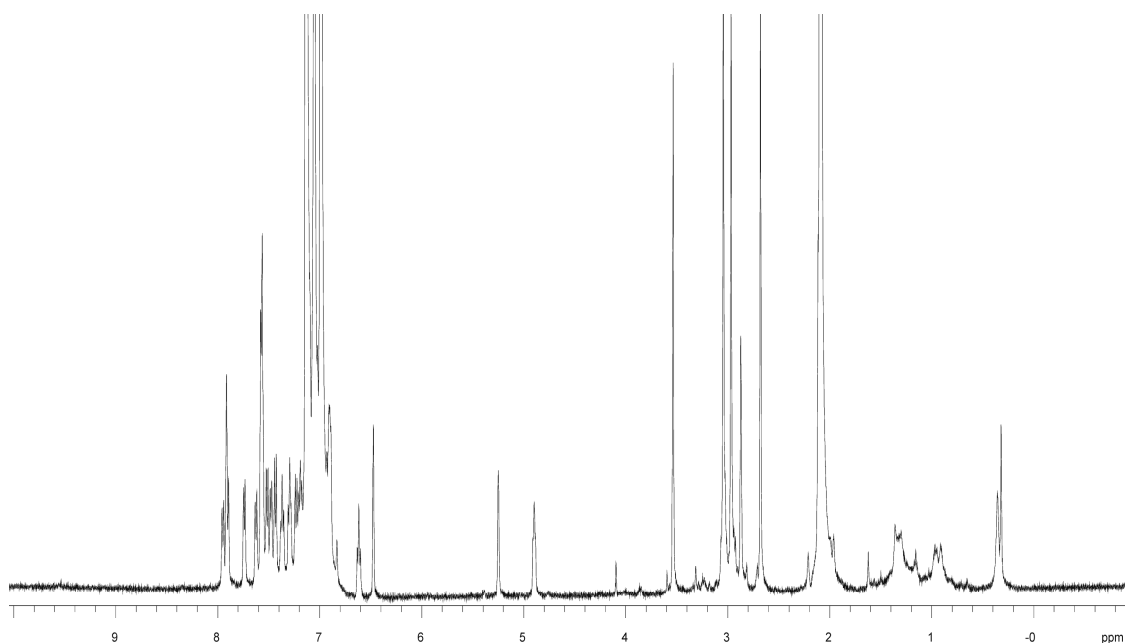




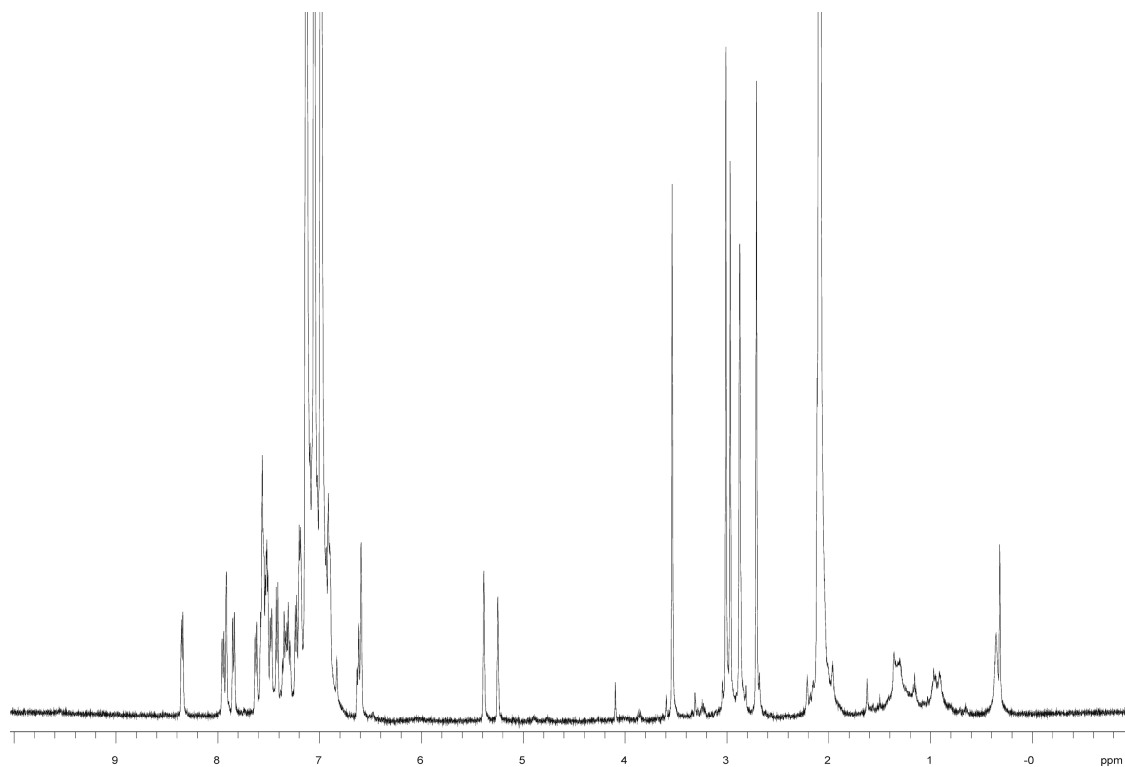
^1H NMR spectrum (500 MHz, toluene- d_8 , $-30\text{ }^\circ\text{C}$) of (Z)-8 before irradiation:



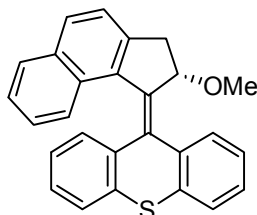
^1H NMR spectrum (500 MHz, toluene- d_8 , $-30\text{ }^\circ\text{C}$) of (Z)-8 after irradiation:



^1H NMR spectrum (500 MHz, toluene- d_8 , $-30\text{ }^\circ\text{C}$) of (Z)-**8** after subsequent heating:



X-ray Crystallographic Analysis of (*S*)-5



At rt, alkene (*S*)-5 (3.0 mg) was dissolved in a minimal amount of a 1:1 mixture of diethyl ether and pentane. The resulting solution was placed into a small glass vial, after which the vial was placed in a larger glass beaker containing pentane. The beaker was covered and left to stand for several days, during which slow diffusion of the solvents allowed the formation of crystals of (*S*)-5. The crystal used in the X-ray diffraction experiment was a small cut fragment which was cleaved from a large coagulated and in different directions grown crystal chunk. This crystal diffracted weakly, so a 30.0 second exposure time for each image was used.

A. Crystal data and details of the structure determination of alkene (*S*)-5.

Moiety_Formula	C ₂₇ H ₂₀ OS
Formula_Weight, g.mol ⁻¹	392.52
Crystal system	orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
a, Å	7.7954(15)
b, Å	14.349(3)
c, Å	17.845(4)
V, Å ³	1996.1(7)
Θ range unit cell: min.-max., deg; reflections	2.69 - 27.54 ; 2645
Formula_Z	4
SpaceGroup_Z	4
Z' (= Formula_Z / SpaceGroup_Z)	1
ρ _{calc} , g.cm ⁻³	1.306
<i>F</i> (000), electrons	824
μ(Mo K α), cm ⁻¹	1.78
Color, habit	colorless, cut fragment
Approx. crystal dimension, mm	0.29 x 0.15 x 0.11

B. Data collection

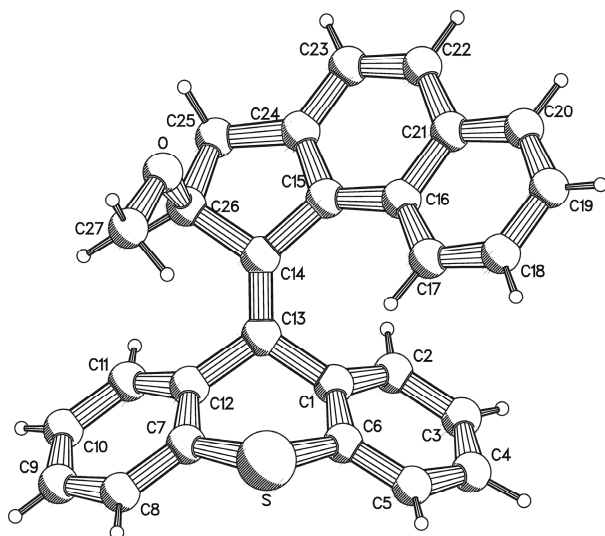
Radiation type; λ, Å	Mo K α , 0.71073
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Monochromator	Graphite
Measurement device type	Bruker SMART APEX
	CCD area-detector diffractometer
Detector Area resolution (pixels / mm)	4096 x 4096 / 62 x 62 (binned 512)
Temperature, K	100(1)
Measurement method	ϕ - and ω -scans
θ range; min. max., deg	2.69, 25.02
Index ranges	h: -9 \rightarrow 9; k: -17 \rightarrow 16; l: -21 \rightarrow 21
Min.- Max. absorption transmission factor	0.9397 - 0.9806
Frames	1800
X-ray exposure time, h	17.9 (30.0 sec / frame)
Total data	14068
Unique data	3526
Data with criterion: ($F_o \geq 4.0 \sigma(F_o)$)	2696
$R_{int} = \Sigma [F_o^2 - F_c^2(\text{mean})] / \Sigma [F_o^2]$	0.0725
$R_{sig} = \Sigma \sigma(F_o^2) / \Sigma [F_o^2]$	0.0742

C. Refinement

Number of reflections	3526
Number of refined parameters	342
Final agreement factors:	
$wR(F^2) = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$	0.0832
Weighting scheme: a, b	0.0391, 0.0
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ And $P = [\max(F_o^2, 0) + 2F_c^2] / 3$	
$R(F) = \Sigma (F_o - F_c) / \Sigma F_o $ For $F_o > 4.0 \sigma(F_o)$	0.0429
Absolute-Structure parameter Flack's x	0.02(9)
GooF = $S = [\Sigma [w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ n = number of reflections p = number of parameters refined	0.971
Residual electron density in final Difference Fourier map, e/Å ³	-0.33, 0.26(5)
Max. (shift/ σ) final cycle	0.001
Average (shift/ σ) final cycle	<0.001

Perspective *PLUTO* drawing of (*S*)-**5**, showing the configuration of the asymmetric unit:



Perspective *ORTEP* drawing of (*S*)-**5**. All atoms are represented by their displacement ellipsoids drawn at the 50% probability level; hydrogen atoms have been omitted to improve clarity:

